ON THE RAMAN SPECTRA OF CARBON DISULPHIDE, BENZENE, CHLOROFORM AND CARBON TETRACHLORIDE IN DIFFERENT STATES AND AT DIFFERENT TEMPERATURES.*

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Plates XIII and XIV.

(Received for publication, March 18th, 1936.)

ABSTRACT. The Raman spectra of carbon disulphide benzene, chloroform and carbon tetrachloride have been investigated in the solid state at the temperature of liquid air. Some new lines in the neighbourhood of the Rayleigh line have been observed in each case. It has also been observed that some changes take place in the intensities, widths and frequency shifts of some of the Raman lines of single molecules of these substances with the lowering of temperature. In the case of carbon disulphide, the satellite 648 cm^{-1} vanishes at the low temperature. This is shown to be in confirmation of the theory put forward by Placzek to explain the origin of this line. The properties of some of the Raman lines of benzene have also been investigated experimentally in the liquid and vapour states and the results obtained for different states and at different temperatures have been discussed. In the case of chloroform, the twofold degeneracy of each of the lines 262 and 762 is observed to be spilt up at the low temperature. In the case of carbon tetrachloride, each of the lines 760 and 789 becomes very sharp at the low temperature. These results are discussed from theoretical point of view.

§ 1. INTRODUCTION.

It has been previously observed by the present author that the Raman spectra of naphthalene and diphenyl ether in the solid state can be easily photographed by using a crystalline aggregate instead of single crystals which were used by Gross and Vuks.[1] It has also been observed [2] that the positions and relative intensities of the new Raman lines of solid naphthalene discovered by Gross and Vuks depend greatly on the temperature of the substance. An attempt has been made to study the Raman spectra of carbon disulphide, benzene, chloroform and carbon tetrachloride in the solid state and at the temperature of liquid air in the same method as employed in the case of naphthalene. It was observed from an examination of the spectrograms that in each case, besides

* Communicated by the Indian Physical Society.

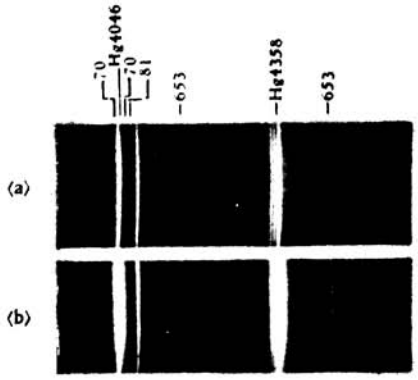
some new lines characteristic of the solid state, the spectrograms also show some changes in the properties of the Raman lines of the single molecules of these substances with the lowering of temperature. A comparative study of the Raman spectra of these substances has therefore been made at different temperatures in different states and the results have been discussed in the present paper in the light of the existing theories.

§ 2. EXPERIMENTAL.

A quantity of carbon disulphide was distilled in vacuum and the colourless pure distillate was transferred to a cleaned pyrex tube which was finally sealed hermetically. The tube was immersed slowly in liquid air contained in a transparent Dewar vessel. The liquid solidified into a semi-transparent mass. The Raman spectrum of this solid mass was photographed in the usual way, a very dilute solution of quinine sulphate being used to absorb the mercury lines on the shorter weve-length side of $\lambda 4047$ and thus to prevent photochemical decomposition. An exposure of about three hours was sufficient for recording the Raman lines with proper densities on Ilford Golden Isozenith plates. The Raman spectra of benzene, chloroform and carbon tetrachloride were also recorded in the same way, the same filter being used in the case of the first two substances in order to cut off the 3650Å group of Hg lines. Each of these latter three substances, when solidified in the above method, becomes a white mass which is more opaque than solid carbon disulphide. The Raman lines, however, are so intense that they are not masked by the strong continuous background produced by stray light. The Raman spectrum of solid carbon disulphide recorded in the above method was remarkably free from continuous background.

On examining the spectrogram due to solid benzene, some changes in the properties of the Raman lines of single molecule were observed to take place with the change of state of the substance and therefore it was thought worth while to study the Raman spectrum of benzene vapour also. The Raman spectrum of benzene vapour at 210°C and at a pressure of about 14 atmospheres was recorded in the same method as employed previously,[5] and exposure of four days being necessary to photograph some of the intense lines with sufficient densities. Also, for comparison, the Raman spectrum of liquid benzene at this temperature and pressure was recorded using proper time of exposure. The Fuess glass spectrograph used in the previous investigations was also used in the present investigation and the width of the slit was the same and about 20μ throughout this investigation.

In order to arrive at a definite conclusion regarding the change of width of the lines with change of temperature and state, the Raman spectra of liquid carbon disulphide and liquid chloroform at the room temperature as well as of



Raman spectra of carbon disulphide.

(a) In the solid state at low temperature.

(b) In the liquid state at the room temperature.

liquid carbon tetrachloride at the room temperature and at about 200° C were recorded using the same width of the slit as in the case of the solid state.

Microphotometric records of the spectrograms were obtained with a Moll's microphotometer.

§ 3. RESULTS AND DISCUSSION.

Carbon disulphide.

The spectrogram obtained with solid carbon disulphide at the temperature of liquid air is reproduced in Plate XIII along with that for the liquid state at the room temperature. It will be observed from a comparison of the two spectrograms that in the case of the solid state, there are two new sharp Raman lines at 70 cm^{-1} and 81 cm^{-1} of which the former is even much more intense than the Raman line 653 cm^{-1} and the latter is very feeble. The line 70 cm^{-1} on the anti-Stokes side is also quite intense. Since these two lines are totally absent in the case of the liquid state, they are characteristic frequencies of the solid state. It is very striking that the new line 70 cm^{-1} is as intense as the Raman lines of rhombic sulphur. In the latter case, the line characteristic of the solid state is at 85 cm^{-1} and therefore the frequency shifts of the two lines observed in the two cases are comparable. The line 85 cm^{-1} of rhombic sulphur is not considered to be due to lattice oscillation in the true sense of the term but it is supposed to be due to the vibration of the S_{16} molecule.[4] The origin of the lines 70 cm^{-1} and 81 cm^{-1} of solid carbon disulphide can also be explained in the similar way. The sharpness of these lines probably suggests that these lines are due to intermolecular vibrations in small polymerised groups of molecules. Since it has been observed in the case of sulphur that the frequency shifts of the lines due to S_8 molecule in solution remain unchanged when S_{16} molecules are formed in the crystals, it can be expected that the frequencies of the Raman lines of CS_2 molecule will remain practically unchanged when in the solid state, polymerised groups are formed and some new lines appear. Actually, it is observed that the line 655·5 cm^{-1} is only shifted to 653 cm^{-1} in the solid state at the low temperature.

Another significant fact is also observed in the Raman spectrum of carbon disulphide at the low temperature. The satellite 648 cm^{-1} of the principal Raman line 653 cm^{-1} is totally absent and the line 653 cm^{-1} is very sharp at the low temperature. This disappearance of the satellite at the low temperature is actually expected from the point of view put forward by Placzek[5] regarding the origin of this satellite. Placzek's explanation is based on the hypothesis which Fermi first applied in the case of carbon dioxide, that owing to the influence of anharmonicity there may be displacement of terms and mixing up of "proper functions" when the terms are accidentally so close to each other that the distance between them is of the order of the coupling energy. In the case of

carbon disulphide there is an intense Raman line at 655·5 cm^{-1} and another weaker line at 796·3 cm^{-1}, the former being accompanied by a feeble satellite at 648·5 cm^{-1} and the latter by another satellite at 810·9 cm^{-1}. The term scheme of the CS_2 molecule obtained according to the above hypothesis is shown diagrammatically in figure 1. If x_2 be the interval between the first two and x_3, that between the last two of the four lines mentioned above,

$$x_2 = 140{\cdot}8 \text{ cm}^{-1} \text{ and}$$
$$x_3 = 162{\cdot}4 \text{ cm}^{-1}.$$

From the relations

$$x_3^2 = \Delta^2 + 16P^2 \quad (1)$$

and $$x_2^2 = \Delta^2 + 32P^2 \quad (2)$$

where $$\Delta = \nu_1 - 2\nu_2$$

and P depends on coupling energy, the values of Δ and P are found to be equal to $-115{\cdot}2$ and $20{\cdot}2$ respectively. ν_1 and ν_2 are the frequencies of the total symmetric and the antisymmetric deformation oscillations respectively. The values of Δ and P given above are slightly different from those given originally by Placzek taking the frequency shift of the satellite to be 642·5 cm^{-1}. Later investigations by Langseth and others[6] and by Rao[7] have, however, shown that the correct value is 648·5 cm^{-1}.

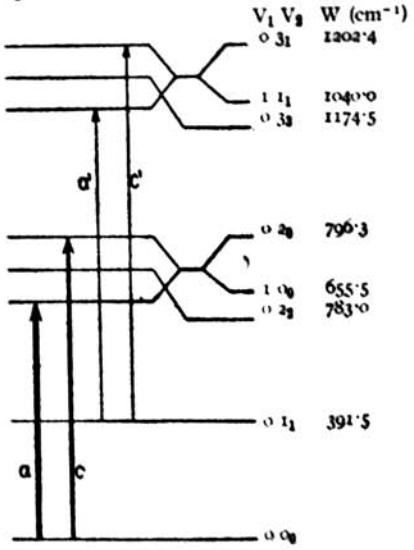


FIGURE 1.

It can be seen from figure 1 that the satellite is produced by the transition from the state $V_1 = 0$, $V_2 = 1$, $s = 1$ to the state $V_1 = 1$, $V_2 = 1$, and $s = 1$, where V_1 and V_2 are the quantum numbers of the two modes of vibration

mentioned above and s is the azimuthal quantum number which varies from $+V_2$ to $-V_2$ and can have only odd or even values according as V_2 is odd or even. The intensity of the satellite, therefore, depends on the population in the initial state, $V_1=0$, $V_2=1$, $s=1$. Since the energy of this state is only 391·5 cm^{-1}, the population in this state at the room temperature is fairly large and therefore, the satellite has appreciable intensity at the room temperature. At the temperature of liquid air, however, the percentage of molecules in this state is only about 1/50 of the percentage in the same state at the room temperature. Hence, the line being fairly weak at the room temperature, vanishes at the lower temperature. This observed fact thus corroborates the view mentioned above regarding the origin of the line.

The satellite 810·9 is also found to be absent at the lower temperature but as it is very weak at the room temperature, no such definite conclusion can be drawn from its disappearance at the low temperature as in the case of the other line 648·5.

Benzene.

Three new Raman lines are observed in the case of solid benzene at the temperature of liquid air, having $\Delta\nu$ equal to 81, 98 and 124 cm^{-1} respectively, of which the first and the third are sharp lines while the second one is a broad band. Gross and Vuks[8] reported two lines at 63 cm^{-1} and 108 cm^{-1} for single crystals of benzene. The temperature of the crystal is not mentioned by the said authors but probably it is a few degrees below the melting point of the substance. Evidently, these two lines become a little sharper and are shifted to 81 and 124 cm^{-1} respectively and also another new band at 98 cm^{-1} appears when the temperature of the solid is lowered till that of liquid air is reached. The new lines characteristic of the solid state observed in the case of benzene and naphthalene, at both the low temperature and approximately at the room temperature are given in table I for comparison.

TABLE I.

Temperature within a few degrees from 0°C		Temperature of liquid air	
benzene	naphthalene	benzene	naphthalene
63 cm^{-1}	42 cm^{-1}		
108 „	71 „	81 cm^{-1}	80 cm^{-1}
	102 „	98 „	
	116 „	124 „	120 „
			142 „

It will be observed from table I that at the low temperature, the frequency-shifts of two of the lines due to benzene coincide respectively with those of the two lines of naphthalene. This is probably due to the fact that the lines are produced by oscillations of benzene nuclei against each other in groups of molecules, these groups being rigid to the same extent in the two cases at the low temperature. The shift of one of the lines from 63 cm^{-1} to 81 cm^{-1} and that of the other from 108 cm^{-1} to 124 cm^{-1} owing to the lowering of the temperature seem to be too great to be explained from the point of view that these lines are due to lattice oscillations. The appearance of a new line at 98 cm^{-1} at the low temperature is also not consistent with the latter hypothesis.

Some changes in the properties of some of the other Raman lines of benzene are also observed to take place with the change of temperature and state. The results obtained for different states and temperature in the case of a few prominent Raman lines of benzene are tabulated in table II. The frequencey shifts are given in wave numbers and are correct only within $\pm$ 1 cm^{-1}. The approximate relative intensities of the lines are given in parentheses.

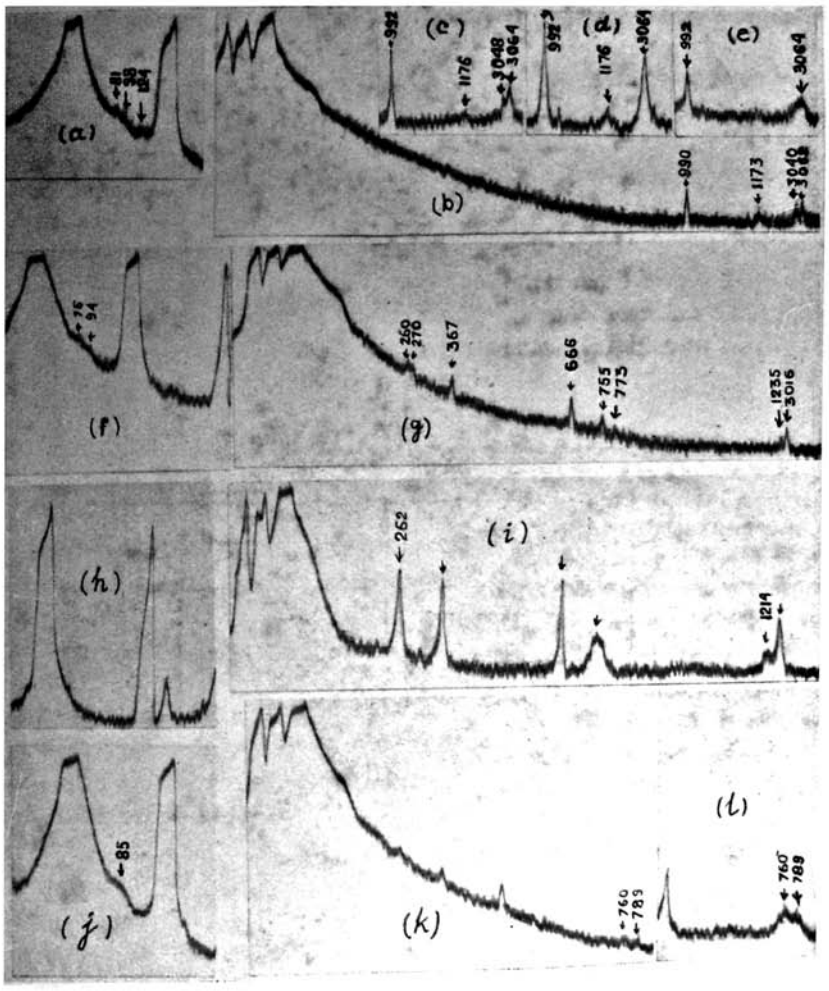
TABLE II.

Benzene.

Solid at liquid air temperature	Liquid at 30°C	Liquid at 210°C	Vapour at 210°C
990 (4)	992 (4)	992 (4)	992 (3)
1173 (1)	1176 (½)	1176 (ob)	1176 (oob)
3040 (1)	3048 (½)	3052 (ob)	faint and very broad not resolved from 3064
3062 (2)	3064 (2)	3064 (2)	3064 (1½)

Microphotometric records of the spectrograms are reproduced in plate XIV.

The Raman spectrum of solid benzene at −150°C was studied also by Epstein and Steiner.[9] He observed that $\Delta\nu$ of each of the lines 984, 992, 1176 and 1584 is lowered by 2 to 3 cm^{-1} at the low temperature. The results of the present investigation confirm those obtained by Epstein and Steiner in the case of the two lines 992 and 1176. The other two lines being faint could not be studied in the present investigation. It will be observed from table II that the line 3048 is shifted much more with the lowering of the temperature than the other lines mentioned above. The width as well as its intensity seem to depend on the temperature of the substance. At the temperature of liquid air, the line is quite



Microphotometric records of the Raman spectra.

⟨a⟩ & ⟨b⟩ Solid C_6H_6 at low temp.
⟨c⟩ Liquid C_6H_6 at room temp.
⟨d⟩ " " " high "
⟨e⟩ Benzene vapour at 210°C
⟨f⟩ & ⟨g⟩ Solid $CHCl_3$ at low temp.
⟨h⟩ Liquid CCl_4 at room temp.
⟨i⟩ " $CHCl_3$ " "
⟨j⟩ & ⟨k⟩ Solid CCl_4 at low temp.
⟨l⟩ Liquid CCl_4 at room temp.

sharp and intense. At the room temperature it is less intense and a little broader. In the case of the liquid state at 210°C it is very broad and feeble and in the case of the vapour at 210°C it is still weaker and diffuse. This line is due to the antisymmetric oscillation of the H-atoms. It is remarkable that the line 3064 due to the total symmetric oscillation of the H-atoms remains practically in the same position in all the stages and at all the temperatures while the line 3048 undergoes considerable changes in width intensity and position with the change of state and temperature of the substance. It is quite evident from close examination of the spectrograms that the increase of width is associated with the rotation of the molecules. When in the solid state there is no rotation of the molecules, the line 3040 is as sharp as the line 3062 and the apparent increase in its intensity at the lower temperature is partly due to the fact that the whole intensity is distributed over a very small width which the line possesses at the low temperature. The disappearance of the line 1176 in the case of the vapour seems also to be partly due to a large increase in its width in this case. This line also is sharper and more intense at the temperature of liquid air than at the room temperature. The shift of the lines 992 and 1176 observed with the lowering of the temperature however, is not an effect of temperature, but is an effect of the change from liquid to the solid state as can be seen from the fact that the positions of these lines remain practically the same for the liquid and vapour states and throughout a range of temperature of about 200°C. Epstein and Steiner have suggested that in the solid state, the C—C bond is slightly loosened causing a slight diminution in $\Delta\nu$ of the Raman line due to total symmetric vibration. An alternative explanation may, however, be offered that these shifts are due to formation of weakly polymerised groups. It is well known that the line 992 is shifted only slightly in some cases even when the benzene nucleus chemically combines with some other groups to form different molecules. Most probably the shift of the lines 992 and 1176 as well as the increase in the intensity of the latter are due to slight deviation from the centro-symmetrical structure of the molecule caused by intermolecular forces at the low temperature.

Chloroform and Carbon tetrachloride.

The Raman lines observed in the case of solid chloroform and solid carbon tetrachloride at the temperature of liquid air are given in table III along with those for the liquid at the room temperature for comparison.

It will be observed from table III that there are two new Raman lines at 75 cm^{-1} and 94 cm^{-1} in the case of solid chloroform and in the case of solid carbon tetrachloride these two lines form a wide band at 85 cm^{-1}. These lines are due to characteristic vibrations of the solid state which are not so sharply

TABLE III.

Chloroform.		Carbon tetrachloride.	
Solid at low temperature.	Liquid at room temperature.	Solid at low temperature.	Liquid at room temperature.
75(1)		85(1b)	
94(1)		219(2)	299(3)
263(1s)	262(4)	314(2)	314(3)
270(1s)		459(3)	459(4)
467(2s)	367(5)	760(0)	760(1½d)
666(4s)	666(6)	789(0)	789(1½d)
755(1)	762(3B)		
773(0)	1214(3)		
1235(0)	1441(1)		
3016(2s)	3016(4)		

quantised in the case of the symmetrical tetrahedral CCl_4 molecule as in the case of benzene or carbon disulphide, although the melting point of carbon tetrachloride is very near to that of benzene. Since the intensity of the wing accompanying the Rayleigh line due to liquid carbon tetrachloride is quite negligible in comparison with that due to liquid chloroform, and on the other hand, both these substances in the solid state and at the low temperature give new Raman lines of the same intensities and in the same position, it seems that these lines have no connection, whatsoever, with the wing observed in the liquid state. Microphotometric records of the spectrograms due to solid $CHCl_3$ and CCl_4 are reproduced in plate XIV.

In the case of chloroform the line 262 is observed to be split up into two sharp lines 260 and 270 of equal intensities at the low temperature. Also the line 762 is observed to be split up into two lines 755 and 773, the intensity of the latter being much smaller than that of the former. Both the lines 262 and 762 are due to twofold degenerate oscillations. It seems that in the case of the line 262, the degeneracy is not complete in the solid state and therefore, two lines of equal intensities are observed. Although the line 262 is slightly broader than the other sharp line 664 at the room temperature, its total width is much smaller than the separation of the two components observed at the lower temperature. Also, the centre of gravity of the two components is different from that of the line 262. It is quite clear from the values of $\Delta\nu$ of the components observed at

the low temperature that the frequency of one of the two modes of oscillations increases at the low temparature, the other remaining constant and thus there is a splitting up of the line. The splitting up of the line 762 into two components at the low temperature, is, however, of different nature from that in the case of the line 262. The component 773 in this case is not of the same intensity as that of the component 755. It is quite possible that in this case at the room temperature, the width of the band 762 being about 20 cm^{-1}, some portions of the band owe their origin to the transitions from some initially excited vibrational state to other higher vibrational states as observed in the case of the satellite 648·5 of the principal Raman line of CS_2. As the temperature is lowered, the intensity of these portions diminishes in the same way as in the case of the satellite 648·5 explained in the previous sections, and thus at the low temperature, the intensity of the other portion of the band remaining the same, two lines, one as intense as at the room temperature and the other very feeble, are observed.

The line 1214 of chloroform is observed to be shifted to 1235 at the low temperature. The shift of this line as well as the splitting up of the line 262 at the low temperature is probably due to the formation of molecular complexes as suggested in other cases in previous sections.

In the case of solid carbon tetrachloride also, some significant fact has been observed. The two lines 760 and 789 each of which is broad and diffuse at the room temperature becomes very sharp at the low temperature. These lines are observed to broaden out to a great extent when the temperature of the liquid is raised to about 200°C. The two components observed at the low temperature are of equal intensities as also at the room temperature. It is well known that in the case of the CCl_4 molecule, the condition $\nu_1+\nu_3=\nu_4$ is satisfied, where $\nu_1=459$ cm^{-1}, $\nu_3=314$ cm^{-1} and $\nu_4=773$ cm^{-1}. There is, therefore, perturbation and displacement of the terms according to Fermi's hypothesis discussed previously and the line 773 is split up into two lines 760 and 789. Each of the two lines should be accompanied by satellites which owe their origin to transitions from initially excited states. As there are a series of such excited states strongly populated at the room temperature, the satellites are not resolved from the lines but only make the lines broad. When at the low temperature these satellites disappear, each of the lines becomes sharp.

Investigations of the Raman spectra of the simple molecules in the solid state at the low temperature are in progress and will be reported later on.

The author's grateful thanks are due to Prof. D. M. Bose for his kind interest in the work.

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